Equilibrium Properties of a Partially Ionized Plasma*

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A model for a partially ionized, partially dissociated plasma has been formulated using known theoretical concepts to describe both bound and free electron states, internal molecular degrees of freedom and Coulomb interactions. It has been applied to a system of particles arising from the hydrogen molecule. The Coulomb interaction is treated in the classical Debye approximation. However, a distance of closest approach between ions and electrons depending on the kinetic energy of the electrons is included to avoid the short-range divergence of the Coulomb potential. The kinetic energy of the free electrons is calculated from the partition function for a perfect Fermi gas. The vibrational and rotational motion are treated in the harmonic oscillator and rigid rotor approximation with the number of energy levels counted for a given electronic state depending on the dissociation energy of the state. A volume dependence of the bound electronic energy eigenvalues is included by considering the effect of surrounding particles as a confinement of a given particle to a spherical box of variable size. For the counting of the bound electronic states, a given state is bound until its energy increases to zero due to confinement. From the partition function for the entire system, the free energy is calculated. By a minimization of the free energy of the system, the equilibrium composition as a function of temperature and volume is obtained. Then not only can thermodynamic quantities be calculated, but it is believed that a reasonable approximation to the correct balance of molecular, ionic and free electronic states is achieved over a wide range of v-T space. Consequently, regions where incomplete ionization and dissociation are important are delineated. In addition, for different regions of v-T space, the relative contributions of charged particle interaction of the nonclassical behavior of electrons, of internal degrees of freedom and of translation to the total energy of the system can be determined.

INTRODUCTION

CONSIDERABLE progress has been made in using diagram methods to derive the equilibrium properties of systems of charged particles.[1] This approach is of particular interest theoretically for its rigor and generality. In principle one proceeds from fundamental laws to exact expressions for the macroscopic properties of arbitrary systems. These expressions ideally take the form of rapidly converging infinite series whose terms are tractable definite integrals. However, this ideal has not yet been attained even for a two-component plasma of electrons and protons. To calculate the properties of multicomponent systems, we have therefore adopted another procedure, a "model" approach, involving many *ad hoc* assumptions based on physical intuition.

In this model a multicomponent system is a collection of subsystems which are molecules, atoms, ions and free electrons. The interactions of electrons and nuclei within these subsystems is taken into account in their internal electronic, vibrational, and rotational partition functions. Electronic eigenvalues are made functions of the volume per subsystem. The functional dependence is based on that of the eigenvalues of a hydrogen atom in a spherical box.[2] The free electrons are treated as a perfect Fermi gas. Electrostatic interactions among charged particles are calculated in the Debye[3] approximation, modified to distinguish between bound and free electrons. For this purpose, ions are regarded as single particles with an effective net charge; the free electron cloud around any positive charge center has zero density within a sphere whose radius depends on the average kinetic energy of the free electrons.

Interactions within the subsystems contribute terms to the partition function which are analogous to classes of localized interactions in the diagram formalism which have not yet been evaluated. Their inclusion in this model extends the applicability of the calculation to the dilute, low-temperature region. In addition, the inclusion of pressure ionization, i.e., the disappearance of bound states with increasing density, assures reasonable behavior in regions of intermediate densities and temperatures. Thus this method allows the calculation of equilibrium properties over a different range than the more rigorous approaches now being studied.

With this model there is a direct indication of the relative importance of various interactions in different density-temperature regions. For example, regions where the concentration of multiparticle subsystems is important can be determined. Also the relative contributions to the free energy from Coulomb interactions, electron degeneracy, and internal degrees of freedom can be ascertained. Such information is very helpful in deciding which aspects of the model need most to be improved. Thus an analysis of the results from a set of assumed interactions serves as a guide to an improved model.[4] It is important that new results can be obtained from an improved model with relatively little additional effort. It thereby becomes feasible to test one's intuitive ideas of the relative importance of various physical effects and particle groupings. Ultimately, the quan-

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[1] J. E. Mayer, J. Chem. Phys. **5**, 67 (1937); E. W. Montroll and J. E. Mayer, J. Chem. Phys. **18**, 626 (1941); E. Meeron, J. Chem. Phys. **26**, 804 (1947); **28**, 630 (1958); H. L. Friedman, Molecular Phys. **2**, 23 (1959); **2**, 190 (1959); T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959). E. W. Montroll and J. C. Ward, Phys. Fluids **1**, 55 (1958); A. E. Glassgold, W. Heckrotte, and K. M. Watson, Phys. Rev. **115**, 1374 (1959); H. Levine, Phys. Fluids (to be published); H. E. DeWitt (to be published).

[2] S. de Groot and C. A. ten Seldam, Physica **12**, 669 (1946).

[3] Discussion of Debye-Hückel Theory in Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, New York, 1952).

[4] In this sense, the model described here is in part an improved version of an earlier model. See G. M. Harris, J. Chem. Phys. **31**, 1211 (1959).

titative utility of this method of calculating the properties of multicomponent systems will rest on agreement with experiment.

In the next section is presented a more detailed description and a brief general discussion of the model which is currently incorporated in a working computer program. It is followed by a presentation and discussion of some of the results obtained when the method is applied to a system of particles arising from the hydrogen molecule.

II. MODEL AND METHOD OF CALCULATION

The system considered is an equilibrium distribution of atomic, ionic, and molecular species arising from one mole of original molecular substance. The *ad hoc* assumptions of the model are all contained in the approximations used to calculate the free energy of the system. The free energy is calculated as the sum of the contributions from the translation of the classical nuclear subsystems, from the translational motion of perfect Fermi electrons, from the internal degrees of freedom of the subsystems, and from a modified classical electrostatic interaction between charged particles. Interactions between neutral particles are neglected, and we consider only small molecules. The calculated Helmholz free energy is minimized with respect to the concentration of each independent component. The equilibrium distribution of the species so obtained is then used to calculate all thermodynamic quantities of interest.

A. Model—The Free Energy Contributions

1. *Translation of Perfect Classical Particles:*

This free energy, F_1, is given exactly by

$$F_1 = kT\sum_i N_i \ln N_i - kT[(\tfrac{3}{2})\ln kT + 6.974 + \ln MW + \ln v] \times \sum_i N_i - (3kT/2)\sum_i N_i \ln M_i,$$

where N_i = number of molecules of species i per molecule, M_i = atomic weight of ith species, v = volume (cc/g), kT is in electron volts, and MW = molecular weight of the original nuclear species.

2. *The Electronic, Vibrational, and Rotational Partition Function*

Experimental data, referred to a common zero of energy, was used to obtain energy eigenvalues for the bound electronic states of each component. For the H atom, the electronic energies were made functions of the volume by assuming each atom to be in a spherical box of a size equal to the average volume per particle in the system.[2] For more complicated components, approximate expressions were formulated, based on the results for the hydrogen atom. Appendix I describes the details of the analytic expression used for each species. When the size of the box was such that the energy of a given bound state was zero, that state was no longer counted. Hence, in addition to the energy eigenvalues, the number of bound electronic states for each component is also a function of the volume and is finite for any finite volume. The harmonic oscillator and rigid rotor approximations were used for the vibrational and rotational partition functions. The number of these states was determined from the dissociation energy of the given electronic state. Thus the total internal partition function for a given component is given by

$$Q_i = \sum_{k=1}^{k_{\max}(v)} \sum_{l=0}^{l_{\max}(ki)} \sum_{j=0}^{j_{\max}(l)} (2j+1) g_{ki} g_{ki}(R) \times \exp\{-[E_{ki}(v) \times W_{ki} l \times B_{ki} j(j+1)]/kT\},$$

where $E_{ki}(v)$ = energy of kth eigenstate of species i at volume v, g_{ki} = degeneracy of kth electronic state, W_{ki} = vibrational frequency of kth electronic state, l = vibrational quantum number, B_{ki} = rotational constant of kth electronic state, j = rotational quantum number, and $g_{ki}(R)$ = fractional weighing factor used to avoid discontinuity in Q as a function of volume; $g_{ki}(R) \neq 1$ only for the last state counted, which is the one of highest negative energy. The cutoff of the vibrational and rotational states is determined by the relationship

$$Do_{ki} = W_{ki} l + B_{ki} j(j+1),$$

where Do_{ki} is the dissociation energy of kth electronic state of the ith species, and $l_{\max}(j=0) = Do_{ki}/W_{ki}$ with a $j_{\max}$ determined for each l. Then the total internal free energy is

$$F_2 = -kT\sum_i N_i \ln Q_i.$$

3. *Perfect Quantum Electron Gas*

The free energy of a perfect Fermi gas is given by

$$F_3 = N_e kT[\nu - (\tfrac{2}{3}) I_{\frac{3}{2}}(\nu)/I_{\frac{1}{2}}(\nu)],$$

where ν is the chemical potential g/kT and

$$I_n(\nu) = \int_0^\infty x^n dx/[1+\exp(-\nu \times x)].$$

The $I_{\frac{1}{2}}$ integrals are related to the electron density by the normalization condition

$$I_{\frac{1}{2}}(\nu) = \frac{N_e}{V(kT)^{\frac{3}{2}}} \frac{h^3}{4\pi(2m_e)^{\frac{3}{2}}},$$

where N_e is the number of electrons.

Through this last equation the quantity (ν) is implicitly given in terms of the specified variables (N_e, V, T). Hence given (N_e, V, T), we can find $I_{\frac{1}{2}}(\nu)$, ν, and $I_{\frac{3}{2}}(\nu)$. For this purpose we have used a four-term asymptotic expansion for $\nu > 4$, the published tables[5] relating these quantities for $4 > \nu > -4$, and the classical expression for $\nu < -4$. We thereby calculate F_3 to within 0.3% for all values of (N_e, V, T).

[5] J. McDougall and E. C. Stoner, Trans. Roy. Soc. (London) **A237**, 67 (1938).

4. *Electrostatic Free Energy* (F_4)

According to the Debye-Hückel model, the contribution to the free energy due to electrostatic interactions is

$$F_4 = -2\pi^{\frac{1}{2}}e^3\sum_i(N_i z_i^2)^{\frac{3}{2}}\tau(\kappa a)/3(VkT)^{\frac{1}{2}},$$

where N_i is the number of particles of charge z_i, a is the distance of closest approach of the centers of 2 ions, and

$$(\kappa a) = 3[\ln(1+\kappa a) - \kappa a + \tfrac{1}{2}(\kappa a)^2]/(\kappa a)^3,$$
$$\kappa^2 = 4\pi e^2\sum N_i z_i^2/VkT.$$

This expression includes a contribution from the interaction of positive ions with all electrons acting as classical charged particles. As a result, if used with arbitrary a it would allow electronic states with a continuum of negative energies decreasing without bound to minus infinity in the limit $a \to 0$. However, the free energy contribution from the bound state interactions of electrons and nuclei has already been included quantum-mechanically and is in fact given by F_2. Therefore we want to treat the interactions of free charged particles only by the Debye-Hückel method. Free electrons are defined as those of positive total energy. The total energy of a free electron is calculated assuming that all free electrons have the same kinetic energy $\bar{E} = kT[I_{\frac{3}{2}}(\nu)/I_{\frac{1}{2}}(\nu)]$ which is the average energy per particle in a perfect Fermi gas. It is also assumed that the potential energy of an electron about a positive charge center is due only to its interaction with that center; although, to be more consistent, the Debye-Hückel potential ought to be used. Then the potential energy of an electron at a distance r_i from a center of charge z_i is $V(r_i) = z_i e^2/r_i$. The quantity a in the Debye expression is interpreted as the distance between the center of an electron and a stationary ion for which the total energy of the electron is zero, i.e., $\bar{E} + V(a_i) = 0$. Thus we obtain $a_i = z_i e^2/\bar{E}$ giving a dependence of the potential energy of the electrons on their kinetic energy through the variable distance $a_i(T,v)$.

We have applied the electron-positive ion cutoff radius (a) to all pairwise interactions. However, the distance of closest approach of like particles should be zero, since the total energy is always positive for repulsive Coulomb interactions. By thus underestimating the repulsive interactions, we obtain a larger net attractive Coulomb energy than we should.

5. *Consistency of the Free Energy Formulation*

In this model two different kinds of distances have been defined which should be consistent. They are the average radius per particle, R, used to calculate the energy of the bound electronic state in a spherical box and the ionic radius, a, used in the electrostatic free energy F_4. The condition $a < R$ means that the system is dilute enough for the free electron to be the required distance away from any one particle and still be within the particle volume. However, for $a > R$ an electron cannot be outside the excluded volume of any one particle without being within that volume for another. The quantity a has meaning only for positive ion-electron interactions. Defining R' to be an average radius per positive ion, in a volume-temperature region where $a/R' > 1$, the assignment of bound electrons to one or the other of a few small subsystems becomes a questionable approximation. In such a region larger interacting clusters must be considered. By calculating the quantity a/R' as well as $I_{\frac{1}{2}}$, and the four contributions to the free energy at every point in a specified temperature-volume grid, the general area of applicability of this model can be determined.

B. Method of Calculation

At each temperature and volume the free energy is minimized with respect to the relative concentrations of all the independent species assumed to be present in the system. The conditions of charge neutrality and conservation of each kind of nucleus reduces the number of independent particle concentrations to $X = N - (A+1)$, where N is the total number of species assumed present and A is the number of different nuclei. In the electronic partition function, the energies and the number of states are dependent on the average volume per particle. Also, in the electrostatic free energy the ionic radii are volume dependent through the dependence of the kinetic energy of a Fermi gas on particle density. Thus, the free energy has a complicated concentration dependence. For this reason the minimum value of F is found most conveniently by a direct search in a finite grid of the independent concentration variables. A 704 code was developed to do this for specified temperature-volume points. A systematic search over each grid size is made by varying 1 through X concentrations simultaneously in turn. Then, by repeatedly decreasing the grid size, a minimum value of F with an accuracy of 1 part in 10^5 is obtained together with the composition corresponding to this minimum. This, then, is the equilibrium composition of the system.

Once the free energy and equilibrium composition of the system are obtained for a given temperature and volume, the pressure and entropy of the system are calculated to a precision of 0.1% in the same code by a three-point numerical differentiation from the relationships

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N_i,T} \quad \text{and} \quad S = -\left(\frac{\partial F}{\partial T}\right)_{N_i,V},$$

where the N_i are the equilibrium concentrations of the N species present. Then the internal energy, $E = F + TS$, the Gibbs free energy, $A = F + PV$, and the enthalpy, $H = E + PV$, are all directly calculated.

C. Specific Application of Model

The model just described has been applied to the calculation of the properties of a multicomponent system

arising from a hydrogen molecule. Six species were assumed to be present: H_2, H_2^+, H, H^-, H^+, and free electrons. In the calculation of F_2 the energies of the two stable states of both H_2^+ and H^- were used. Of the infinite set of bound states possible for an isolated H atom, only 37 states are bound in the maximum size spherical box considered in this calculation, i.e., a specific volume of 4×10^{-20} cc/molecule. For H_2 we included the two Rydberg series of singly excited states which terminate in the two stable states of H_2^+. In addition, all doubly excited states with energies between the ground states of these two series were included.

As noted previously, the energy of a hydrogen-like orbital is known exactly as a function of the volume of a confining sphere. For the other species an approximate relationship between bound state energies and volume was used. The electronic energy of each state was represented as a sum of the energies of one-electron hydrogen-like orbitals with different effective nuclear charges. These were chosen to reproduce the excitation and ionization energies of the isolated species when these were known. In the remaining instances, the energies of the isolated molecules were estimated by interpolation. For many excited states, molecular constants used in the rotational and vibrational energies were also estimated by interpolation. Appendix II gives the details of these procedures.

For the electrostatic free energy, F_4, the ions, protons, and electrons were all treated as single particle charges with the same pairwise distance of closest approach. The total free energy was minimized in a grid of four independent concentration variables for a given set of temperature-volume points. The calculations cover the temperature range $0.025\leq T\leq100$ ev; and the volume range 0.1 to 12 000 cc/g.

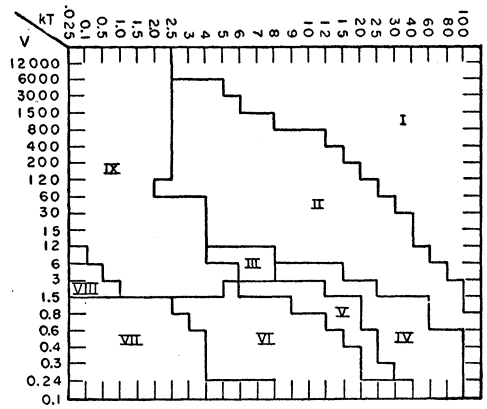

FIG. 1. Schematic representation of the behavior of H_2 system. kT is given in ev, and V in cc/g. The normal solid density of H_2 is 12 cc/g.

III. RESULTS

A. Regions of Importance of the Partial Free Energies

Figure 1 is a schematic representation of the behavior of the H_2 system over the entire v-T region considered. Table I explains and defines the meaning of the Roman-numeral designations of the figure. To define the regions of Fig. 1, we arbitrarily label free energy contributions of less than 1% as negligible, and greater than 10% as strong. If a quantity other than the free energy had been used as a basis for comparison, somewhat different definitions would apply. It should be noted that there is no region of a perfect quantum gas and in all regions except the one that is called metallic, Coulomb interactions are more important than electron degeneracy.

TABLE I. Interaction regions of Fig. 1.

Region	Description	Definition
I	Perfect classical gas of point particles	$\lvert\Delta F_2\rvert$,[a] $\lvert\Delta F_3\rvert$,[b] $\lvert F_4\rvert<0.01\lvert F_1\rvert$
II	Classical gas of interacting point particles	$10>\lvert F_4\rvert>1$[c]; $\lvert F_2\rvert$, $\lvert\Delta F_3\rvert$ negligible[d]
III	Classical interacting gas with internal degrees of freedom	$10>\lvert F_4\rvert$, $\lvert\Delta F_2\rvert>1$; ΔF_3 negligible
IV	Quantum gas of interacting point charges	$10>\lvert F_4\rvert$, $\lvert\Delta F_3\rvert>1$; ΔF_2 negligible
V	Quantum gas of strongly interacting point charges	$\lvert F_4\rvert>10$; $10>\lvert\Delta F_3\rvert>1$; ΔF_2 negligible
VI	Highly degenerate gas of strongly interacting point charges	$\lvert F_4\rvert$, $\lvert\Delta F_3\rvert>10$; ΔF_2 negligible
VII	Metallic. Comparable potential and kinetic free energy	$\lvert F_3\rvert\simeq\lvert F_4\rvert$; F_1, ΔF_2 negligible
VIII	Molecular solid	$\lvert\Delta F_2\rvert$largest; F_1, F_4, ΔF_3 negligible
IX	Perfect classical gas with internal degrees of freedom	$10>\lvert\Delta F_2\rvert>1$; F_4, ΔF_3 negligible

[a] Included in F_2 is a factor 15.833 N_1 which is just a correction for the zero of energy from isolated protons and electrons to the ground state of the H_2 molecule. In calculating the contribution of the electronic vibrational and rotational states to the free energy, this factor is subtracted.
[b] F_3 is the total kinetic free energy of the electrons. To determine the effect of the quantum statistics only the difference in the value of F_3 for classical electrons and the calculated value is significant, i.e., $\Delta F_3=F_3-F_3$ (classical). It is the magnitude of ΔF_3 relative to F_1 which is used to determine the degree of degeneracy of the electrons. The spin degeneracy of the electron remains in the classical limit and is hence not included in the quantum effect.
[c] The range of value of the F's are given in percent relative to $\lvert F_1\rvert$, the classical kinetic free energy.
[d] Negligible means $<1\%$ of $\lvert F_1\rvert$.

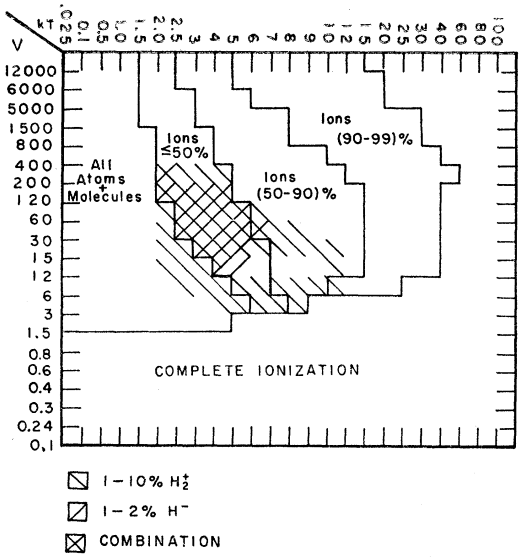

FIG. 2. Schematic representation of composition variation. "Ions" refers to protons and electrons. "All atoms+molecules" refers to H_2, H, H_2^+, and H^-.

B. Composition Variation

Figure 2 illustrates the composition variation with volume and temperature. The most striking result of this model is the effect of particle density on the degree of ionization. The system is completely ionized for all temperatures at infinite volume. If the bound state electronic energies were independent of volume, then the number of free electrons would decrease monotonically as a function of density. This would occur since the free electron translational energy increases and the number of states per energy interval decreases as the density increases. However, with this model, the bound state energies also increase with density and the number of bound states decreases due to the confinement distortion of the bound state electronic wave functions. Thus, at some density, free electron states can once again be favored relative to bound states and the percent ionization can increase with density. We do indeed find this behavior characteristic of "pressure ionization". The percent ionization increases from infinite volume to a minimum at some finite density where it then increases to complete ionization at large density. The present model for the volume dependence of the bound electronic eigenvalues predicts that there can be no bound states at any temperature for volumes smaller than fifteen-fold liquid density (0.8 cc/g). At higher densities, we have a totally ionized plasma. For low temperatures, i.e., $T\leq 7$ ev, total ionization occurs as a nearly discontinuous increase in the degree of ionization with increasing density. This is most extreme for $T=1$ ev where we have nothing but H_2 molecules and H atoms up to almost fifteen-fold liquid density and complete ionization at slightly greater density. For the range $T=1.5$-5 ev there is a gradual decrease in ionization to zero with a nearly discontinuous rise from zero to complete ionization. At $T=6$ and 7 ev, there is a gradual decrease in ionization but the minimum percent ionization is not zero. The rise from the minimum to complete ionization is still almost discontinuous. Finally at $T\geq 8$ ev, there is a smooth decrease in ionization to a minimum with a smooth increase to complete ionization. The higher the temperature the larger the minimum amount of ionization and the lower the volume at which complete ionization occurs. Finally at $T\geq 50$ ev there is complete ionization for all densities studied.

Figure 3 illustrates the effect of density on the degree of ionization in these various temperature regions. It is believed that the discontinuity which occurs at the lower temperatures is the result of the omission of larger clusters of subsystems. With the present model an electron is either free in the entire system or it is bound in a 2, 3, or 4 particle sybsystem. Forced to maintain one or the other of these rather extreme distributions, the system as a whole has no way of freeing electrons in a continuous manner. The presence of pseudoparticles of the type: H_n^{+z} with $n\geq 3$ and $n>z>0$ which free one electron per fraction of nucleus and in which bound electrons are not severely localized, would allow a more gradual transition from molecules to ions. At higher temperatures, due to ionization and dissociation, the presence of such large systems would be negligible. This fact accounts for the smooth variation of the number of free electrons with density, obtained for $T>8$ with the present system.

The degree of ionization as a function of temperature is also affected by the description of the bound states. The number and energy of the bound states depends not only on total volume, but also, through particle density, on temperature. Since the number of particles increases with temperature, the energy of the bound states increases and the number of bound states decreases as the temperature is increased at constant volume. Thus the ordinary temperature effect on ionization is enhanced. This takes place continuously for compressions below four-fold liquid density, where the

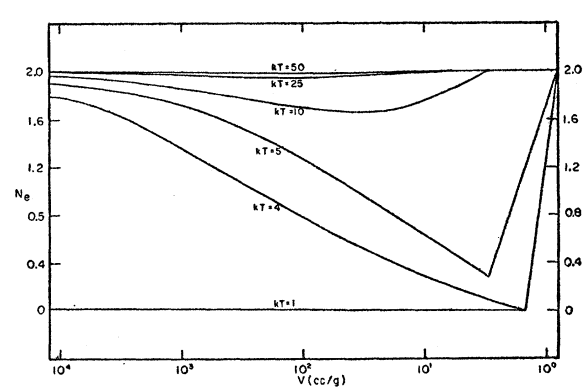

FIG. 3. Volume dependence of the degree of ionization. $N_e=2$ corresponds to 100% ionization.

degree of ionization is a smoothly increasing function of the temperature. At two-fold liquid density the last of the bound states for H^- disappears, but since this is always present in trivial amounts it has little effect on the rate of ionization. At four-fold liquid density, the ground state of the H atom disappears at $T=8$ ev. At $T=9$ ev, the last bound states of H_2 and H_2^+ disappear, giving complete ionization. This leads to a rapid, continuous rise in the number of free electrons from 25% of all electrons at $T=7$, to 72% at $T=8$, to 100% at $T=9$. At eight-fold liquid density, the last bound states of all species disappear together at $T=5$ where the number of free electrons rises abruptly to 100% from a negligible 0.75% of all electrons at $T=4.5$. For higher densities there is complete ionization at all temperatures. These rapid changes are the coincidental results of the increase in particle density with temperature and the increase with particle density of the bound state electronic energies. The resulting abrupt composition changes resemble phase transitions, but no physical meaning can be attached to them on the basis of this calculation.

C. Discussion and Evaluation of Results

At all volumes and temperatures for which the composition and free energy were calculated, the entropy, internal energy, enthalpy, Gibbs free energy and pressure were also obtained. The reliability of these results is better measured by the accuracy of the pressure than the free energy, since the volume derivative is more sensitive to the deficiencies of the model and does not contain the arbitrary constants of the free energy. Our estimate of the accuracy of the calculated pressure is summarized schematically in Fig. 4. This estimate was made by a qualitative theoretical analysis of the limitations of the model and by comparisons with both experimental data and other theoretical calculations. Qualitative information concerning the limitations of the calculation was obtained by comparing our approximate model with the more exact considerations provided by quantum statistical theory. This information was used together with the numerical results to define regions of reliability of the model. For example, comparison with exact theory might indicate that Coulomb interactions are poorly represented by our model. The results delineate regions of strong Coulomb interactions thereby allowing us to define regions of questionable accuracy. Because of the lack of other independent data, it happens that for a large portion of v-T space this process affords the only available means of evaluating the results obtained.

1. *Limitations of the Model*

In a rigorous derivation of the equilibrium properties of a hydrogen plasma, one considers a two-component system of electrons and protons which experience only Coulomb interactions. All possible combinations of

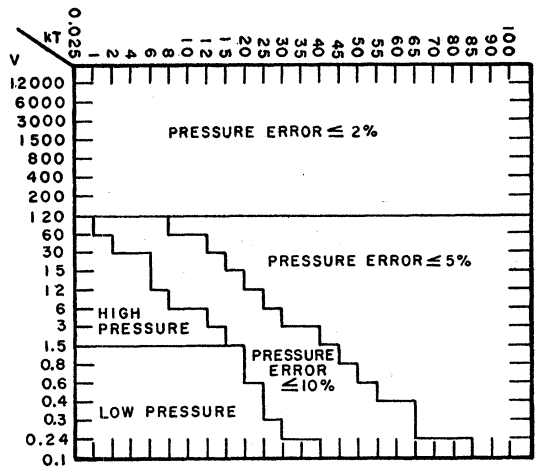

FIG. 4. Schematic representation of pressure accuracy.

simultaneous interactions among them would be evaluated. Because an exact solution of this problem is extremely difficult, much effort has been spent in developing approximate methods involving various expansions of the potential. In these expansions an attempt is made to find systematic groupings of the interactions between the particles based on the kinds of particle groups one expects to be important. One convenient classification of these groups is into bound or unbound systems. A group of particles is considered bound if there is a high probability that the distance between any two particles in the group is small compared to the radius of a sphere containing a mole of such groups. A group is unbound if any two particles in it have a high probability of being separated by a distance comparable to the radius of such a sphere. If we do not restrict the number of particles in these groups then we get a complete description of the system, in which Coulomb interactions alone occur. However, in this calculation we consider only the groups symbolized by H_2, H_2^+, H^-, H, H^+, and e^-, in the hope that these groups represent the most important bound state systems. By including the electronic, vibrational and rotational energies of these species, we are considering to some approximation the Coulomb interactions between the fundamental particles which resulted in the formation of these systems. In order to describe the unbound states of these groups and to account for the interactions of larger groups of fundamental particles, we have introduced several further approximations, some of which involve non-Coulomb interactions. There are also approximations in our description of the bound states of H_2 and H_2^+. We assume the separability of electronic, vibrational and rotational energies, we use the cutoff harmonic oscillator and rigid rotor models for molecular vibration and rotation, and we use only approximate electronic energies for the excited states of H_2. These approximations are most significant in regions VIII and IX of Fig. 1, where mostly atoms and molecules are present.

Another approximation in the calculation is the use of the Debye-Hückel model for the collective Coulomb interactions of the four charged species assumed present. As is well known, this approximation is accurate only in the limit of low charge density and high temperature. Moreover, when both the electron degeneracy and the Coulomb interactions are significant, there are additional errors due to the breakdown of the classical separation of kinetic and potential energy, and the neglect of quantum effects due to the wave nature of the electrons and the Pauli exclusion principle. No attempt has been made to include exchange effects. However, we make a crude correction for the dependence of the potential energy of the electrons on their kinetic energy, and thereby for diffraction effects, through our interpretation of the cutoff radius in the Debye expression. Since the Debye result with zero ionic radius is recovered in the limit of infinite charge density, the Coulomb interaction energy is given accurately only when this energy and the electron degeneracy are both small as in regions II, III, and IV of Fig. 1. It should be progressively worse, the greater the charged particle density at a given temperature and the lower the temperature at a given density, i.e., the order of error in the regions of Fig. 1 is V<VI<VII.

In any model which, like the present one, includes only a few of the possible bound state systems, it is necessary to approximate in some way the Coulomb interactions of the remaining groups of particles. Part of this is accomplished by the use of the Debye model for the simultaneous interaction of all the charged groups present. To approximate the remaining interactions among the subgroups to form larger groups, one common method is to assume some form for the potential of interaction which is a function of the configuration of the subgroups considered as point particles. This approach is inexact since the energy of the entire group is not uniquely defined by the configurations of the centers of mass of the individual subgroups. However, this should lead to a reasonable description of the system in density-temperature regions where the dimensions of the individual bound state systems are small compared to their center-of-mass separations. This method then can describe only weakly attractive or repulsive forces, neglecting completely bound states of the larger groups. The present calculation approximates the interactions between the small subgroups by a density-dependent spherical confinement of the bound electrons of each group, which leads to a perturbation of their energy eigenvalues. We have, then, nothing in our model which corresponds to weak attractive forces, such as Van der Waals forces. In addition, we overestimate the repulsive interaction by the extreme confinement of the bound electrons in a hard-wall sphere whose volume is equal to the volume per group. However, the model does give a qualitatively correct description of the effect of density on the electron distribution. As the individual subgroups approach one another, they interact in such a way as to cause a redistribution of electrons resulting in delocalization. The reason for this is that a forced confinement of the electrons increases their kinetic energy more rapidly than their potential energy. Thus the minimum energy configuration subject to the density constraint must be associated with the maximum possible delocalization. This delocalization is synonomous with the loss of identity of the small subgroups. In the present model, we have allowed for the disappearance of the subgroups by a gradual decrease in the number of bound states. A bound state is no longer counted when its energy has increased to zero. This criterion is roughly equivalent to the exclusion of a state when its average volume exceeds the volume per group. While this gives us a qualitatively correct description of the density effect on the number of free electrons, our quantitative results are likely to have significant error due to our crude approximation of the energy-volume dependence. The approximation should be most reasonable when the perturbation due to the surrounding groups is small. Thus it should be valid over much of region VIII and IX of Fig. 1 but becomes poorer as the density increases.

2. *Comparison and Discussion of Results*

(a) For a gas at normal volume down to a tenth of liquid density, it is believed that the calculated pressure is good to within a few percent in the entire temperature range studied. This estimate is based on the following considerations:

(1) There is agreement with experimental heat capacities and pressures from the $T=0.025$ points at these volumes.[6] Since only H_2 molecules are present at this temperature, this indicates that the model provides a reasonable description of the rotational and vibrational degrees of freedom. As a further test of the treatment of vibration, the harmonic oscillator eigenvalues were replaced by those obtained from a Morse potential. This change had almost no effect on the pressure and heat capacity, indicating that the detailed description of the vibrational states is not a significant factor in determining the results. This result, plus the fact that a previous calculation[4] with no cutoff gives very different answers shows that the counting of the vibrational states is much more important than their exact eigenvalues. Also, since we find that H_2 dissociates mainly in the ground electronic state, errors in our estimates of the excited states of H_2 can not lead to significant error.

(2) The electrostatic interactions never exceed 5% and the system is always classical in this region so that the Debye approximation is likely to be fairly accurate.

It seems that at present this method gives the only reasonable description of a multicomponent system in

[6] Experimental values taken mainly from *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1928), Vol. III, p. 5.

this region. The Thomas-Fermi statistical model[7] is inapplicable for a dilute gas and the more rigorous diagram expansion methods have not made much progress as yet in regions where two-, three-, and four-particle bound states make the most important contributions to the properties of the system.[1] At temperatures where the system is completely ionized, so that existing diagram techniques can be applied, it is also a perfect classical gas and hence of little interest.

(b) As the density is increased at $T=0.025$, from a fifth of liquid density to twice liquid density, the calculted pressures exceed the experimental values by an amount which increases rapidly from 30% of the experimental pressure to a factor of 25. Only H_2 is present under these conditions, which means that F_3 and F_4 are zero. Since F_1 is exact, the error in the pressure is due entirely to $(\partial F_2/\partial v)$, i.e., to the assumed relation between F_2 and v.

It will be recalled that the energy of a hydrogen-like orbital in a spherical box is almost unperturbed by a change in the radius of the box, down to a small radius. The energy then increases rapidly over a very short interval, producing a similar increase in the magnitude of F_2. Since the population of excited states is always small, this contribution to F_2 is due almost entirely to the volume dependence of the energies of the *ls* orbitals. Furthermore the contribution to F_2 from the ground states of H_2, H_2^+, H^-, and H is proportional to the number of bound groups, being otherwise independent of temperature. Therefore, since the number of bound groups decreases with increasing temperature and other contributions to the pressure increase, both the relative and absolute magnitude of the error in the pressure caused by this aspect of the model goes down as the temperature rises.

At these densities and $T=0.25$, the experimental evidence indicates that the interactions of bound groups strongly affect the pressure. However, in the same way that the effect of F_2 on the calculated pressure becomes small, the relative contribution of other molecular interactions to the pressure must also decrease with temperature. Furthermore, when the system consists mainly of ions, the contribution of Coulomb interactions to F is found to be moderate and the system is classical. As a result of this analysis, a temperature region for this volume range, i.e., $v=3-120$ cc/g can be estimated where the error in pressure is less than 10% and another where the error is further reduced to less than 5%, as indicated in Fig. 4.

Unfortunately, except for the low-temperature experimental data and the normal density Thomas-Fermi-Dirac calculation of Cowan and Kirkwood,[8] there is nothing with which to compare our results on these regions. A comparison with the Cowan-Kirkwood results in Table II show that our pressures are too high at the lower temperatures. That the use of orbitals in a spherical box would lead to excessive pressures was obvious from the outset. While we were interested to discover quantitatively the error incurred, the model was used mainly to achieve pressure ionization in a simple way, and for correct physical reasons.

TABLE II. Comparison of Cowan-Kirkwood (CK) and present calculation H_2 at normal liquid density.

PV/kT \ kT	100	70	50	30	20	10	8	5
CK	2.0	1.90	1.80	1.70	1.65	1.53	1.45	1.40
Present	2.0	1.98	1.96	1.90	1.88	1.96	1.94	1.93

(c) Four- and eight-fold liquid density are special volumes in this calculation since complete ionization occurs as the temperature increases due to the increase in particle density beyond a critical value. These are abrupt changes similar to phase transitions and give a discontinuity in the pressure. At temperatures lower than those required for ionization, the pressures are much too high, due again to the erroneously large dependence of the bound state energies on volume. After ionization, the contribution to the pressure from the Coulomb interactions increases drastically. This is the only region where the quantity a/R' becomes greater than one. The results at these volumes are not to be trusted until the potential energy has again become a moderate fraction of the kinetic energy. For $v=3$ this means a minimum temperature of 10 ev and for $v=1.5$ a minimum temperature of 15 ev. The results of a Thomas-Fermi[7] (TF) calculation are better than ours at the lower temperatures for these volumes. Their pressures at zero temperature are still higher than experiment, but lower than ours. The TF results continue to be lower until 5 ev when ours become lower and stay lower even at 100 ev. This latter comparison indicates that our estimate of the interaction pressure is larger than that in the TF model.

(d) In the region of complete pressure ionization, $v\leq 0.8$ cc/g, the results are very poor at low and moderate temperatures. This is a region of extreme degeneracy and large interactions. Hence the neglect of quantum diffraction and exchange effects and the use of only the Debye term, with a cutoff ineffective for complete ionization, severely limit the applicability of the model. Table III gives a comparison for $v\leq 0.4$ and zero temperature of the results of Gell-Mann and Brueckner,[9] the present calculation, and a TF calculation. If the more rigorous Gell-Mann and Brueckner results are to be taken as most accurate in the region of convergence of their series of terms, then it is apparent that our model severely overestimates the electrostatic interaction

[7] N. H. March, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1957), Vol. 6, No. 21, p. 1. N. Metropolis and J. R. Reitz, J. Chem. Phys. **19**, 555 (1951); R. P. Feyman, N. Metropolis, and E. Teller, Phys. Rev. **75**, 1561 (1949); R. Latter, Phys. Rev. **99**, 510 (1955); **99**, 1854 (1955); J. Chem. Phys. **24**, 280 (1956).

[8] R. D. Cowan and J. G. Kirkwood, J. Chem. Phys. **29**, 264 (1958).

[9] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

TABLE III. Comparison of high-density zero-temperature results of Gell-Mann and Brueckner (GMB).

Calculation \ v(cc/g)	$v=0.4(r_s=1.0)$[a] K.E.[b]	P.E.[b]	P[c]	$v=0.24(r_s=0.865)$ K.E.	P.E.	P	$v=0.1(r_s=0.644)$ K.E.	P.E.	P
Present	28.86	−28.18	1.47	40	−39.5	3.6	72.5	−70.5	17.6
GMB	28.53	−10.89	9.21	40	−15.8	25.8	72.5	−20.0	120
TFD			21.97			59.4			306

[a] $r_s=r_0/a$, where r_0 is the volume per electron and a is the Bohr radius.
[b] Kinetic energy and potential energy in units of electron volts.
[c] Pressure in megabars.

while the TF model underestimates it. Any improvement of our model in this region must come from a consideration of quantum effects on the Coulomb interactions in the completely ionized plasma. In this region the usefulness of our model is extremely limited and the more rigorous calculations have made the most progress. At temperatures where the Coulomb interaction is again a small part of the kinetic energy our results should again become reasonable. In this high density-high temperature region our accuracy is comparable to that of the diagram calculations of DeWitt[1] on the partially degenerate completely ionized plasma.

In summary it is felt that progress has been made in describing the equilibrium properties of a partially ionized, partially dissociated, multicomponent plasma, in regions of v-T space where internal degrees of freedom and bound electronic states are important and in regions of moderate interaction and moderate degeneracy. Under conditions of complete pressure ionization, i.e., high density, low and moderate temperatures, this model is unsatisfactory. At higher temperatures where the kinetic energy terms again dominate, our model, the TF model, and the more rigorous approach appear to be about equally accurate.

APPENDIX I

The Laguerre polynomials provide energies for each hydrogenic state at a discrete set of radii of the confining spherical box. These radii correspond to integral values of the principal quantum number, n. For the lowest energy states no energies can be obtained for finite radii greater than a few angstroms. Nevertheless, except for the ground states of each species, we have used only the discrete data afforded by the Laguerre polynomials together with the energy value at $R=\infty$, to determine a smooth variation of the energies with R:

$$E_{ki}(R)=13.595(Z_{ki}^2/n_i^2)\times\{1-\exp[a_i(R_{0i}/Z_{ki}R-Z_{ki}R/R_{0i})]\},$$

where E_{ki}=energy of the ith bound state of the kth species in spherical box of radius R, Z_{ki}=effective nuclear charge of the ith state of the kth species, R_{0i} =the radius at which the energy of ith state of the H atom becomes zero, a_i=a constant for the ith state of the H atom, and n_i=principle quantum number of the ith state of the H atom. For the ground states, zeros of the more general hypergeometric functions were used[2] to determine more accurately the energy-volume relationship for large radii. This leads to a different dependence of E on R:

$$E_{k(1s)}=13.595Z_{k(1s)}^2[1-X^{-(a+bX)}],$$

where a and b are constants, 2 and 1.16 respectively, and $X=Z_{ki}R/R_{0i}$. This more exact expression for the energy of an H atom in a box then gives a smaller perturbation for large R, and a larger value of $(\partial E/\partial R)$ for box sizes near the region of applicability of the Laguerre polynomials. The more exact relationship was applied only to the ground states since it was thought that before excited states became appreciably populated atoms and molecules would no longer be a significant part of the composition. This is certainly a good approximation for the molecular states and is least true for the states of the hydrogen atom.

APPENDIX II

Each electronic energy was expressed as a sum of atomic hydrogen-like terms having various effective nuclear charges, with one term for each electron present in the molecule:

$$E_{ki}=-\frac{13.595Z_{ki}^2}{n_i^2}f(Z_{ki},R)-\frac{13.595Z_{ki}'^2}{n_i'^2}f(Z_{ki}',R),$$

where the f's represent the volume dependence described in Appendix I. We now give some examples of the procedure used to determine the values of the effective nuclear charge Z_{ki} for various states.

For the $1s\sigma$ state of H_2^+ we set

$$-13.595Z^2(H_2^+,1s\sigma)/n_{1s}^2=\epsilon(H_2^+,1s\sigma)=-15.377,$$

where $\epsilon(H_2^+,1s\sigma)$ is the known electronic energy of the $1s\sigma$ state of H_2^+ relative to the fundamental particles at infinite separation.[10] Since $n_{1s}=1$, we get

$$Z(H_2^+,1s\sigma)=(15.377/13.595)^{\frac{1}{2}}=1.0976.$$

For the $(1s\sigma)^2$ of H_2 we set

$$2\left[-\frac{13.595Z^2(H_2,1s\sigma)}{n_{1s}^2}\right]=\epsilon(H_2,(1s\sigma)^2)=-31.925$$

[10] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), 2nd ed.

and obtain

$$Z(\mathrm{H}_2,1s\sigma)=(31.925/27.190)^{\frac{1}{2}}=1.0836.$$

The calculation of $Z(\mathrm{H}^-,1s^2)$, etc., exactly parallels these examples.

For the Rydberg series starting with the $(1s\sigma,2s\sigma)$ state of H_2 and ending in the $1s\sigma$ state of H_2^+, the eigenvalues were taken to be

$$E(\mathrm{H}_2;\,1s\sigma,n)=\mathrm{E}(\mathrm{H}_2^+,1s\sigma)+E(\mathrm{H},n),$$

where n is the principal quantum number for any one-electron excited state. Application of this expression to the $(1s\sigma,2s\sigma)$ state of H_2 gives an electronic energy of -19.78 ev, while the experimental value is -19.26 ev. To obtain the corresponding vibrational and rotational constants we used the expressions

$$D_0(\mathrm{H}_2;\,1s\sigma,n)=(1-n^{-2})D_0(\mathrm{H}_2^+,1s\sigma)+n^{-2}D_0(\mathrm{H}_2,(1s\sigma)^2),$$
$$W(\mathrm{H}_2;\,1s\sigma,n)=(1-n^{-2})W(\mathrm{H}_2^+,1s\sigma)+n^{-2}W(\mathrm{H}_2,(1s\sigma)^2),$$
$$B(\mathrm{H}_2;\,1s\sigma,n)=(1-n^{-2})B(\mathrm{H}_2^+,1s\sigma)+n^{-2}B(\mathrm{H}_2,(1s\sigma)^2).$$

These expressions give $W=0.350$ ev, $B=4.66\times10^{-3}$ ev for the $(1s\sigma,2s\sigma)$ state of H_2 in comparison with the experimental values, $W=0.321$ ev, $B=4.05\times10^{-3}$ ev. The experimental value of D_0 for this state is not available.

As suggested by Teller's work on H_2^+,[11] only one other Rydberg series appears in the calculation. The series begins with the $(3d\sigma,4s\sigma)$ state of H_2 and ends in the $3d\sigma$ state of H_2^+. The calculation of electronic eigenvalues and vibrational and rotational constants for these states follows exactly the procedure just given.

[11] E. Teller, Z. Physik **61**, 458 (1930).